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The Adsorption of Ammonia by Silica Gel

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY
LEVI YORGEY DAVIDHEISER
BALTIMORE
June, 1922

EASTON, PA.:
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The author wishes to express his thanks and appreciation to Dr. W. A. Patrick under whose instruction this work was carried on for the aid and suggestions received.

I also wish to take this opportunity to extend my sincere thanks to Drs. Frazer, Reid, Lovelace and Thornton for their kind assistance in the laboratory and lecture room.

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THE ADSORPTION OF AMMONIA BY SILICA GEL.

This investigation is a continuation of the studies of Patrick of adsorption of gases and vapors by silica gel. In Göttingen he studied the adsorption of ammonia, sulfur dioxide and carbon dioxide. Since then many improvements in experimental technique have been introduced, as well as radical modifications of the theoretical treatment of the experimental results. The experimental method and an outline of the theoretical views have been given in a paper dealing with the adsorption of sulfur dioxide.[1]

The adsorption of ammonia was studied for a number of reasons. In the first place, this gas, in the measurements made in Göttingen, was found to be more strongly adsorbed than sulfur dioxide although the latter exhibits a higher critical temperature. In the second place, our previous measurements indicated that the behavior of ammonia was anomalous from the standpoint of the rate at which equilibrium was reached. Again, ammonia is extremely soluble in water and it was therefore hoped that by a careful study of its adsorption by silica gel, light would be thrown on the question as to the nature of the small amount of water that is always associated with the gel. Furthermore, in am-

[1] MacGavack and Patrick, *J. Am. Chem. Soc.*, **42**, 946 (1920).

monia we have a gas that has been the subject of numerous careful investigations, and as a result the physical constants, such as vapor pressure, density and surface tension, are very accurately known. This latter point is especially important inasmuch as a knowledge of the above constants is necessary for the testing of our theoretical views as to the course of the adsorption.

In the following measurements of the adsorption of ammonia by silica gel, it will be shown that this gas is not anomalous in its behavior, either from the standpoint of the extent or the rate of the adsorption, the earlier discrepancies being due to the uncertain water and acid content of the gel. Especial study was made of the influence of the water content of the gel on the adsorption, and it was found that small differences produced large variations in the adsorptive ability of the material.

Apparatus.—The experimental method has been described in detail by MacGavack and Patrick.[1] To give an idea of the precision attained, it may be stated that the volume of ammonia was measured to within 0.005 cc., the pressure to within 0.03 mm., and the temperature of the thermostat regulated so as not to vary more than 0.05°.

Material.—The ammonia used was purified liquid ammonia. Commercial ammonia was treated with metallic sodium for one week, and the accumulated gas allowed to escape at intervals of 12 hours. The purified sample was tested by allowing a small stream of the gas to bubble into sulfuric acid contained in a gas buret for 10 minutes; as no residue was shown by this procedure it was assumed that the ammonia was free from permanent gases.

The silica gel was an ordinary commercial sample that was further purified by treatment with nitric acid and a thorough washing with distilled water. When dried in a vacuum of 1 to 5 mm. at a temperature of 300° for 3 hours the gel still contained 5.21% of water, and furthermore an appreciable amount of nitric acid, to which reference will be made later.

Procedure.—The adsorption apparatus was evacuated by means of a rotary oil pump and a Gaede mercury pump, connected in series. Before any gel was put into the adsorption bulb, the apparatus was thoroughly evacuated and then swept out with ammonia and evacuated again until the MacLeod gage showed no pressure after standing under a vacuum for 48 hours. The gel was weighed in the adsorption bulb, which was then directly attached to the apparatus by means of a ground joint, and sealed by mercury. The pumps were always started before the stopcock between the adsorption bulb and the main apparatus was opened, so that the air in the bulb would have less chance to become adsorbed on the walls of the apparatus. The heating of the adsorption bulb was started at the same time, care being taken not to heat the gel to a higher temperature

than that at which it was prepared, so that the water content might not be disturbed. The evacuation was continued until the MacLeod gage showed no pressure, usually from 3 to 8 hours, at a temperature from 290° to 300°.

In the beginning it was found almost impossible to make two determinations that would agree. After a considerable number of measurements had been made at 30°, a few were found to check fairly well. However, a number of measurements made at 40° showed that the gel exhibited greater adsorptive ability at this temperature than at 30°. Such inconsistent and disturbing results led us to stop and thorougly inspect our apparatus and method of procedure. The apparatus was first examined for leaks. It was thoroughly evacuated and allowed to stand for one week, at the end of which the MacLeod gage showed no increase of pressure. The ammonia was again examined and no foreign gases found. Another series of measurements was made at 30° in which great care was taken that all manipulations should be as nearly identical as possible. The electric furnace, in which the adsorption bulb was heated during evacuation, was kept constant and evacuation continued for exactly the same length of time. Under these conditions checks could be made with but little variation. This proved that the gel did not remain constant

TABLE I

EXPERIMENTS AT 0°, 30°, 40° AND 100°

Expt. XX

Temp., 30°; H_2O content, 4.93%; Wt. of gel., 0.5739 g.; D, 0.5939; σ, 18.03; $1/N$, 0.2103; K, 57.30; P_o, 874.90.

P	X/M	V	$P\sigma/P_o$
0.07	26.82	0.034	0.001443
1.009	68.05	0.087	0.020792
37.726	126.66	0.161	0.683757

Expt. XXIII

Temp., 40°; H_2O content, 4.93%; Wt. of gel, 0.5730 g.; D, 0.5769; σ, 16.70; $1/N$, 0.2093; K, 53.53; P_o, 1165.80.

P	X/M	V	$P\sigma/P_o$
0.218	36.42	0.050	0.003123
4.026	77.03	0.101	0.057672
20.987	101.06	0.133	0.300622
61.632	126.25	0.166	0.882887

P = equilibrium pressure in cm. of mercury.

X/M = cc. of ammonia under standard conditions adsorbed per g. of gel.

V = cc. of liquid ammonia adsorbed.

Expt. XXV

Temp., 0°; H_2O content, 4.93%; Wt. of gel, 0.5744 g.; D, 0.6389; σ, 25.94; P_o, 322.10; $1/N$, 0.2116; K, 82.40.

P	X/M	V	$P\sigma/P_o$
0.153	58.77	0.070	0.012321
8.116	123.47	0.147	0.654614
33.494	168.59	0.200	2.697404
58.653	191.99	0.228	4.723902

Expt. XXIX

Temp., 100°; H_2O content, 4.93%; Wt. of gel, 0.5737 g.; D, 0.4589; σ, 6.5 $1/N$, 0.2885; K, 23.07; P_o, 4693.40.

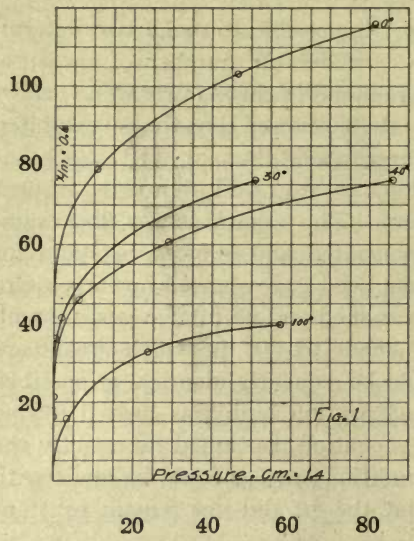
P	X/M	V	$P\sigma/P_o$
2.147	27.05	0.04473	0.00276
13.805	52.22	0.08636	0.01912
41.016	66.62	0.11017	0.05681

P_o = vapor pressure of liquid ammonia.

D = density of liquid ammonia.

σ = surface tension of liquid ammonia.

during evacuation, and especially was this true when the pumps were run for different lengths of time. All the experiments recorded in this paper were made under conditions that allow exact duplication.



In Table I Experiments XX, XXIII, XXV and XXIX are recorded the results of the measurements made at 0°, 30°, 40° and 100°. These results are shown graphically in Fig. 1. Equilibrium was usually reached in from 15 to 30 minutes; nevertheless the ammonia was allowed to remain in contact with the gel for at least 2 hours. As more ammonia was introduced and the pressure increased, the time required to reach equilibrium also increased. If equilibrium was not reached within 2 hours after the introduction of the first amount of ammonia, it served as an indication that the air had not been completely removed from the apparatus. It was found that 3 hours' evacuation with the adsorption bulb heated to 290° was sufficient to remove all the air. All the determinations were made under these conditions. After this treatment it was found that the gel lost 0.28% of its water content. When this treatment was continued for 8 hours 0.487% of the water was removed. The gel upon analysis was found to contain 0.437% of nitric acid, equivalent to 5.23 cc. of ammonia. Of course as the gel lost some of its water content some of the acid also was lost.

Inasmuch as our preliminary measurements showed that the water content of the gel was a most important factor in determining the extent of the adsorption, an effort was made to prepare a gel of low water content. It has previously been thought that the presence of the water was very closely associated with the structure of the material and the removal of the water below 2% was considered undesirable. The subsequent results, however, indicate that such views are unsound and that it is possible to obtain a gel possessing the proper adsorptive structure having only 0.33% of water.

A gel containing 0.33% of water was prepared by heating it in a Pyrex glass tube through which a current of dry air was passed. The tube was gradually heated with a Bunsen flame for 1 hour, and then in the flame of the blast lamp for 2 hours to the fusion point of Py-

rex glass. During this process the gel became perfectly clear and colorless.

After this treatment the gel was tested for its ability to adsorb ammonia. It was rather surprising to find that it was still a good adsorbent for ammonia, adsorbing on an average about 53 cc. less per gram than it did before this drastic treatment. Two isotherms were made, one at 0° and one at 30°. Fig. 3 shows the graph of these determinations as compared with those made before dehydrating the gel. Table II, Experiments XXXI and XXXV show the experimental results.

TABLE II

ACTION OF GEL AFTER HEAT TREATMENT

Expt. XXXI

Temp., 30°; H_2O content, 0.33%; Wt. of gel, 0.5739 g.; D, 0.5939; σ, 18.03; $1/N$, 0.2487; K, 21.33; P_o, 874.90.

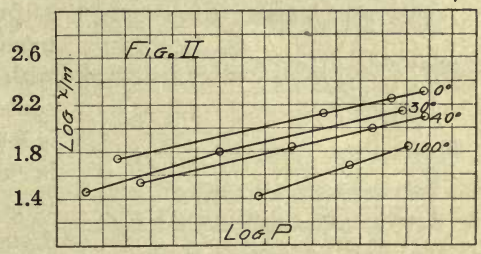
P	X/M	V	$P\sigma/P_o$
1.293	24.49	0.03113	0.026646
8.653	46.00	0.05878	0.178021
18.933	57.08	0.07294	0.390173
36.600	73.50	0.09392	0.754265
59.697	83.01	0.10608	1.23024

Expt. XXXV

Temp., 0°; H_2O content, 0.33%; Wt. of gel, 0.5739 g.; D, 0.6389; σ, 24.94; $1/N$, 0.3948; K, 28.765; P_o, 322.10.

P	X/M	V	$P\sigma/P_o$
3.391	47.85	0.05684	0.273091
6.763	61.35	0.07287	0.544651
13.964	80.54	0.09567	1.124572
46.056	127.50	0.15145	3.708976
61.365	145.44	0.17276	4.941874

It is necessary to mention a phenomenon that was observed with the measurements made at 100°. After 33.64 cc. of ammonia had been brought over 0.5741 g. of gel and the pressure had reached a value of 287.35 mm., it was noticed that there was a gradual increase in the pressure. This increase in pressure continued until at the end of 9 days the pressure in the apparatus was 471.40 mm. Upon cooling the gel to 0°, the pressure immediately dropped to 4.53 mm., while heating again to 100° caused an immediate rise in pressure to the value of 471.40 mm. That this phenomenon is in some way associated with the water of the gel is indicated by the fact that no such behavior as outlined above was exhibited with the gel containing only 0.33% of water.



Discussion of Results.

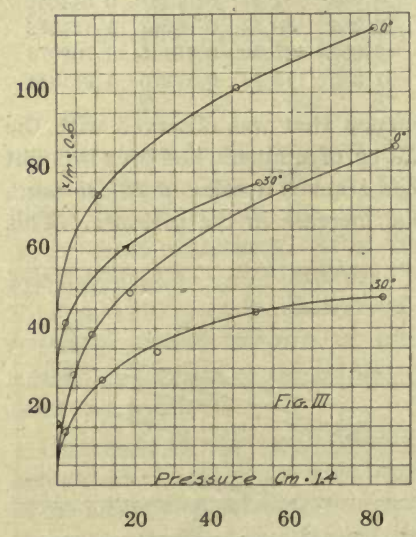
The various isotherms may be very accurately represented by the ordinary empirical adsorption formula, $X/M = KP^{1/N}$. In Fig. 2 are plotted the logarithms of X/M against P, and from the straightness of the lines it is apparent that the above formula accurately reflects the

experimental data. Inasmuch as the sulfur dioxide was also well represented by the same relationship, the comparison of the behavior of ammonia and sulfur dioxide is greatly facilitated by use of the values of K at the same temperature. In the following table are given the values of K for sulfur dioxide and ammonia obtained with a gel of approximately the same water content, 4.8%.

	NH_3	SO_2
	K	K
0°	82.40	29.14
30°	57.30	12.93
40°	53.53	9.75
100°	23.01	1.12

Inasmuch as the significance of K is the number of cubic centimeters of gas adsorbed by 1 g. of gel at a pressure of 1 cm., it is apparent that ammonia is more strongly adsorbed than sulfur dioxide by this particular sample of gel.

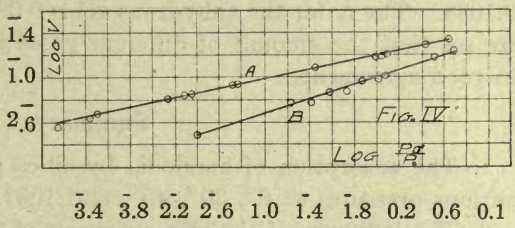
That this result is due to the larger solubility of ammonia in water, is shown by the fact that the value of K for ammonia at 0° decreased from 82.40 to a value of 28.76 when the water content was reduced from 4.88% to 0.33%. While it is true that the adsorption of sulfur dioxide is lessened by a diminution of the water content of the gel, the effect here is not so pronounced as in the case of ammonia. It will be observed that with a gel containing 0.33% water content, the adsorption of ammonia is lower than that of sulfur dioxide in a gel containing 4.87% water. It is our belief that with an anhydrous gel the adsorption of ammonia will be found to be in accordance with its ease of condensation as expressed by its critical temperature.



The above results for ammonia must also be corrected for the acid that is present in the gel. In the beginning it was thought that prolonged washing with distilled water was sufficient to remove all acid, especially inasmuch as the acid diffuses readily through the gel when in the state that it is when washed. Nevertheless, upon collecting the liquid that is driven off from a gel containing 5.21% water by heating to 800–900°, the same was found to require 0.653 cc. of 0.1066 N alkali for the neutralization per gram of gel. This acid would probably not exert an appre-

ciable effect upon an acidic gas such as sulfur dioxide, but would materially affect the adsorption of ammonia.

The above facts illustrate the great need for care when generalizations are drawn concerning adsorption. It is apparent that the amount of ammonia that the gel is capable of taking up depends not only on the capillary structure of the gel, but in addition upon the water and acid content. Before generalizations as to the effect of capillarity on adsorption may be drawn, it is necessary to allow for the solubility of the gas in the water and the amount of ammonia that combines with the acid present.



If instead of expressing the weight of ammonia taken up by a unit weight of gel under a certain pressure, the volume of liquid ammonia adsorbed per gram of gel under its condensation pressure is used, all the isotherms fall on a smooth curve which may be expressed by the equation

$V=K(\frac{P\sigma}{P_o})^{1/N}$. These results are shown in Fig. 4, where will be found plotted the logarithms of the volume of ammonia adsorbed against the logarithms of the condensing pressures $(P\sigma/P_o)$.

A similar result was obtained with the sulfur dioxide measurements where the values of K and $1/N$ were 0.1039 and 0.447, respectively. In the case of ammonia with a gel of 4.88% water content, the equation becomes $V=0.1679\left(\frac{P\sigma}{P_o}\right)0.2105$; while with a gel of 0.33% water content K has the value of 0.0955 and $1/N$ of 0.3588.

At first thought it may be considered strange that the above formula should apply to the adsorption of ammonia when we consider the very large portion of the ammonia that is dissolved in the water of the gel. This behavior is immediately explained, however, from the fact that the solubility of ammonia in water may be expressed by the same formula that is used to express the results of the adsorption of ammonia by silica gel. In other words, as shown by measurements made in this laboratory, the solubility of ammonia in water is well represented by the formula,

$$V=K\left(\frac{P\sigma}{P_o}\right)^{1/N}.$$

It has also been shown that the solubility of sulfur dioxide in water may be well represented by the above formula where K equals 0.0123 and $1/N$ equals 0.91. It is therefore possible to calculate the adsorption

due to the capillary structure alone by correcting, with the aid of the above formula, for the amount of gas dissolved in the water of the gel. Applying this formula, $V=K\left(\frac{P\sigma}{P_o}\right)^{1/N}+0.048\,K'\left(\frac{P\sigma}{P_o}\right)^{1/N'}$, to the measurements of ammonia made with the gel containing 4.8% water, the value of K becomes 0.1147. Doing the same with the measurements of sulfur dioxide, we find that the mean value for K does not differ much from 0.1038. The K for the anhydrous gel is 0.0955. From these experiments we see that the amount of different gases adsorbed due to capillarity is in good agreement.

Summary.

1. The adsorption of ammonia by silica gel has been measured under various pressures at 0°, 30°, 40°, and 100°.

2. The influence of the water content of the gel on the adsorption has been studied.

3. It has been shown that the adsorption of ammonia may be satisfactorily explained on the basis of capillary condensation, provided corrections are made for the amount of the gas that dissolves in the water.

BIOGRAPHY

Levi Yorgey Davidheiser was born at New Hanover, Pa, in 1885. He received his elementary education in the schools of his native village, Boyertown High School and Perkiomen School; from the latter institution he was graduated in 1903. He then took up the teaching profession, in which he continued until 1911 when he entered Ursinus College, from which institution he was graduated in 1914 with the degree of A.B. He again took up teaching. In 1917 he entered the graduate school of Johns Hopkins University, following the subjects of Chemistry, Physical Chemistry and Mathematics. During the year 1918–19 he was employed by the Aetna Explosives Co., Emporium, Pa., as head chemist of the acid laboratories. In the fall of 1919 he again took up his work at Johns Hopkins University, completing his course in June, 1922.

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